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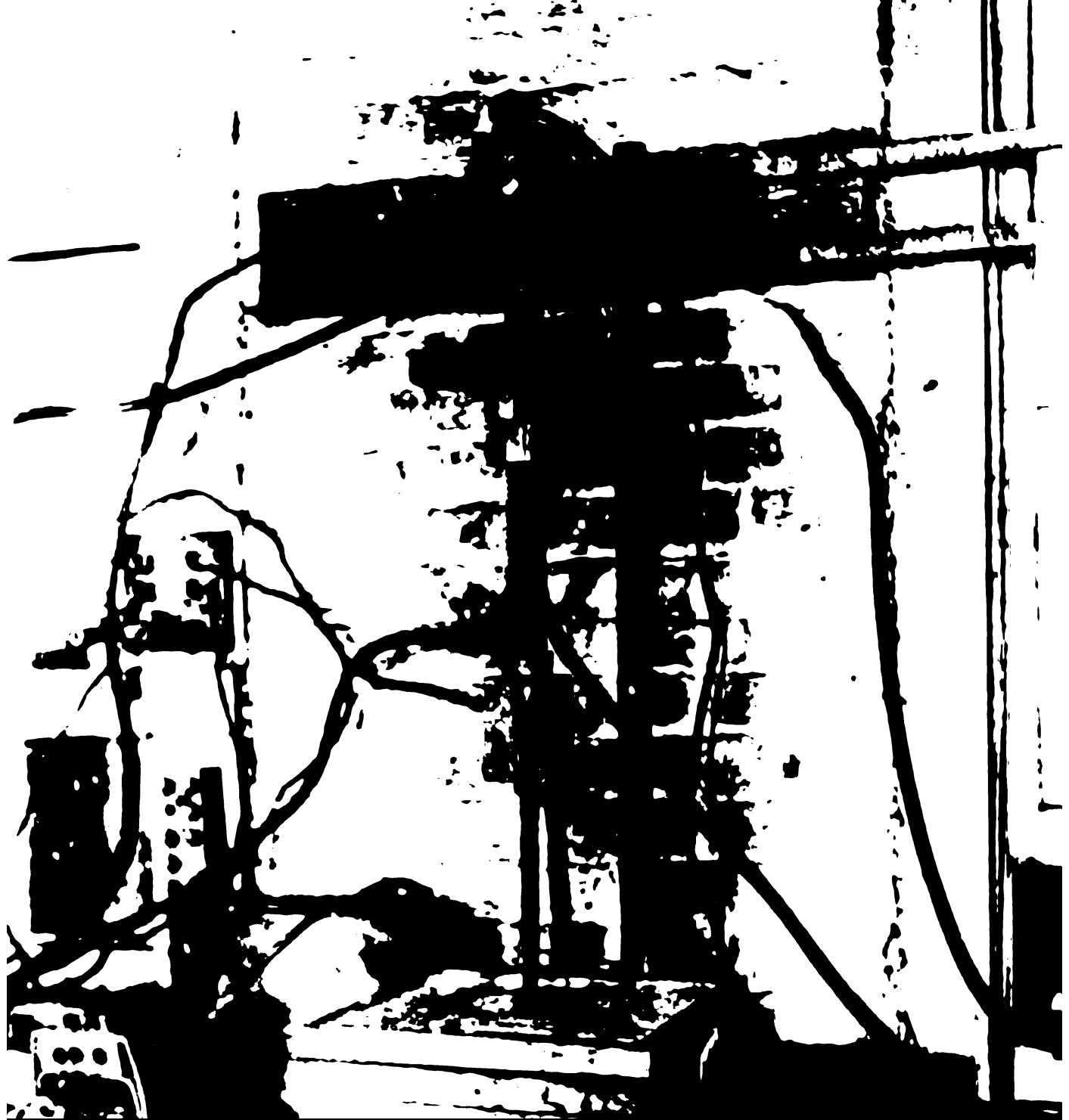
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ELECTROLYTIC PRODUCTION OF  
METALLIC CALCIUM

by

Arden Richard Johnson

A Thesis Submitted for the Degree of  
BACHELOR OF SCIENCE  
Applied Electrochemistry Course

UNIVERSITY OF WISCONSIN

1906



## INTRODUCTION.

Metallic calcium has been known for some time to possess chemical and physical properties which would make it of great value in the chemical and metallurgical industries if it could be isolated from its compounds cheaply. But for almost a century the problem has remained unsolved so far as anything like commercial success is concerned; indeed, to isolate the element in very small quantities on a laboratory scale has proved to be one of the most difficult experiments in the electrolysis of fused salts.

The production of sodium electrolytically from a fused electrolyte is a well established industry though at first sight the process appears to present far greater difficulties than calcium on account of its greater chemical activity and very low melting point, (below that of NaOH from which it is electrolyzed).

Evidently one phase of the calcium problem lies in the characteristic chemical and physical properties possessed by the electrolyte from which the metal is to be electrolyzed, which gives rise to such internal reactions in the bath during electrolysis, as to prevent the deposition of the element. A second phase is the construction of a suitable electrolyzing apparatus out of such materials as will stand the terrific attacks of the very active electrode products (calcium and chlorine) and electrolyte





( $\text{CaCl}_2$ ), at the high temperature of  $800^\circ \text{C}$ :

In the prosecution of this thesis upon the electrolytic production of calcium, two aims have been kept constantly in view:

- (a) To study the chemical and physical changes and phenomena exhibited by the electrolyte during electrolysis.
- (b) To find out the most suitable and durable type of electrolyzing apparatus.



## HISTORICAL.

In the year 1808 metallic calcium was isolated from its compounds for the first time. The conception of a process for obtaining this element, as well as others of the alkaline earth group, is found in that remarkable series of experiments performed by the great scientist Sir Humphrey Davy in the early part of the nineteenth century.

The process of Davy <sup>(1)</sup>, as described in his Bakerian lecture of 1808, was essentially as follows: "The earth (CaO) was slightly moistened, and mixed with one-third of red oxide of mercury, the mixture was placed on a dish of platina, a cavity was made in the upper part of it to receive a globule of mercury of from 50 to 60 g. in weight, the whole was covered by a film of naphtha, and the plate was made positive and the mercury negative, by the proper communication with a battery of 500 cells."

The amalgams obtained in this way, were distilled in U tubes of common glass filled with an atmosphere of inert naphtha vapor. Davy further says: "I found immediately that the mercury rose pure by distillation from the amalgam, and it was very easy to separate a part of it; but to obtain a complete evaporation was very difficult."

After leaving the work of Davy, whose work was truly remarkable for his time, we must pass over a space of 46 years to another pioneer in the field of electrochemistry., Robert Bunsen <sup>(2)</sup>. Bunsen had a theory concerning



the wonderful results which might be obtained by the use of very high cathode current densities, and as stated briefly in his own words was as follows: " The density of the current used for electrolysis- that is, the relation of current volume to electrode area- exerts a most important influence on its chemical effects. The power of the current to overcome (chemical) affinity increases with this density."

By employing as cathode an amalgated platinum wire dipping in a solution of  $\text{CaCl}_2$ , acidified with  $\text{HCl}$ , and contained in a carbon crucible which served as anode, Bunsen claims to have succeeded in obtaining minute quantities of calcium amalgam by using sufficient current density.

As a natural consequence of these experiments, Matthiessen,<sup>(2)</sup> a student working in Bunsen's laboratory in the year 1855, at the latter's suggestion, obtained the metals of the alkaline earths in pure condition by the direct treatment of the fused chlorides. Matthiessen writes: "Although the reduction is easy, it is difficult to obtain the reduced metal in coherent masses, and to separate it from the fused substance. The deposited metals for the most part rise to the surface, by the virtue of their low specific gravity, before they have grown to globules of appreciable size; and there they burn so quickly that it is impossible to collect them." He then advances the following three ideas:



1. "Deposit calcium on platinum or other metallic cathode with which it will form an amalgam, drop off and sink through bath to bottom."
2. "Melt together two chlorides in similar molecular proportions, making a compound of low fusion point, thus hindering the vaporization or solution of deposited calcium. At such temperature as to have thin layer of solid salt on surface."
3. "Separation of calcium below surface of melt on a fine pointed cathode; the metal thus receiving a thin coating of  $\text{CaCl}_2$ ."

It appears that Matthiessen was the first to actually obtain pure metallic calcium by the direct electrolysis of its fused salt. A sufficient quantity of the metal was obtained so that he could describe its chemical and physical properties with approximate accuracy.

After the time of Matthiessen no work of any considerable importance was done until Borchers<sup>(4)(5)(7)</sup> in Germany undertook for the first time to design an apparatus upon the fundamental principles laid down by Bunsen and Matthiessen for the production of calcium upon something like a commercial scale. His three guiding principles were the following:

1. "A high current density of from 323 to 645 amperes per square foot."





2. "A low temperature in the electrolyte."
3. "A high temperature at the cathode."

To fulfill conditions 1 and 3 it will be seen from the diagrams, Plate I, that a needle, or very small iron rod, insulated from the  $\text{CaCl}_2$  container, was used as cathode. The anode was a large carbon rod, or as in later designs, the wall of the container itself. In some of his designs the bath was fused externally. Borchers claims to have gotten a current efficiency as high as 20%, though in most cases it was not greater than 5%. However, this type of apparatus proved a commercial failure for reasons to be pointed out.

Up to 1903 attempts to obtain metallic calcium were made by experimenters other than those mentioned, but in all these cases their efforts were practically without results of importance, either in the discovery of new electrolytes, processes, or designs of apparatus. In May 1903, however, a Mr. Rathenau of Germany made known to the public through a short address before the Bunsen Society, and also by patent, his idea of electrolyzing fused  $\text{CaCl}_2$ , using a carbon anode, and an iron cathode, and pulling the iron rod up out of the bath as fast as calcium deposited on it until finally a calcium cathode, is obtained. This method is the only distinctly new one since the time of Matthiessen, and in the hands of Rathenau and others has given results beyond anything hitherto attained.



Since Rathenan announced his process Joseph Goodwin  
 (14)(18) of Pennsylvania University, and Paul Woehler (17) in  
 Germany, have worked processes for obtaining calcium which  
 embody in all essentials the Rathenan principle, and may  
 justly be regarded as efforts at duplicating the latter's  
 experiments. The apparatus used by Goodwin and Woehler are  
 shown in diagrams 3 and 4, Plate I.

While the work of the three experimenters last named has,  
 no doubt, been excellent, yet Woehler alone attempts to  
 give in his published work any idea of the modus operandi  
 of the bath,- the chemical and physical phenomena which  
 transpire during electrolysis. The actual conditions under  
 which calcium can be obtained, or the effects of different  
 chemical and physical conditions upon the nature of the de-  
 posited calcium, and the influence of the apparatus design  
 upon results, are not discussed.

During the prosecution of this thesis an endeavor has  
 been made to pay particular attention to these important  
 features.

The main efforts to produce calcium seem to have been  
 through the medium of a correctly designed apparatus for  
 electrolyzing, and if we glance over the different de-  
 signs we shall recognize just two different types: First,  
 the apparatus of the Borchers type for utilizing an extreme-  
 ly high current density and consequently obtaining the cal-  
 cium in a molten condition in which it rises to the surface



## PLATE I/

### No.1. Borchers's Apparatus.

- V - Iron container for electrolyte.
- A - Carbon anode.
- C - Iron needle cathode insulated from container.
- S - Shelf under which molten calcium may collect.

### No.2. Borchers's-Stockem Apparatus.

- A - Circular graphite anode.
- C - Iron needle cathode.
- H - Water cooled bottom insulated from anode.
- B - Brick Support.

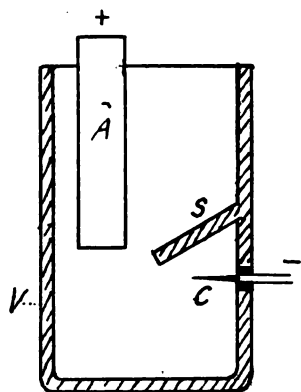
### No.3. Woehler Apparatus.

- A - Graphite anode.
- C - Iron cathode.
- V - Iron electrolyzing vessel.
- V'- Sheet-iron jacket.
- B - Bunsen burner for melting bath.

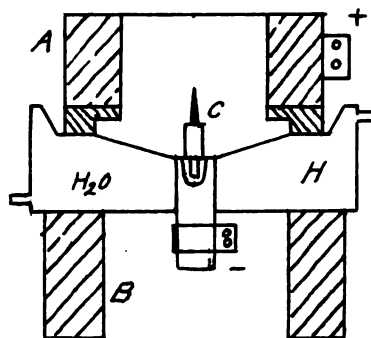
### No.4. Goodwin Apparatus.

- A - Graphite, circular anode container.
- C - Iron cathode.(Fastened to stationery upright screw.)
- P - Water pipes for keeping bottom of vessel cool.
- B - Brick support.

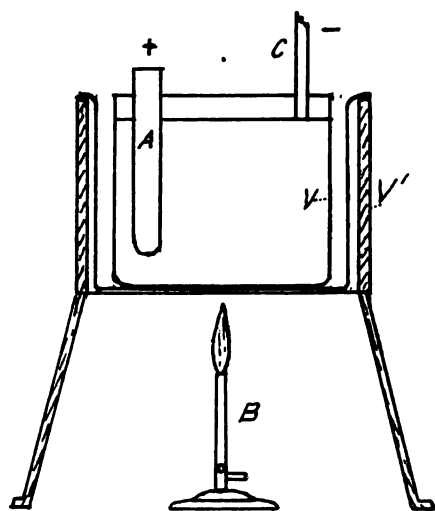




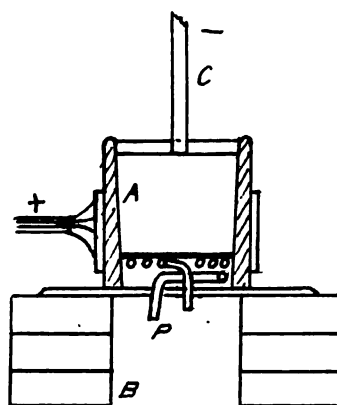
No. I Borchers



No. II Borchers-Stockem



No. III Woehler



No. IV Goodwin

Plate I.





and is skimmed off; and secondly, the Rathenan type, which requires that the calcium come out in a compact form, that is, plated out at a moderately low current density.

#### EXPERIMENTS WITH APPARATUS NO. 1.

In view of the successful results which have been attained by the above mentioned experimenters using the Rathenan type of apparatus, I decided also to begin the study of the electrolysis of  $\text{CaCl}_2$  with an apparatus of this class. Accordingly the design shown in plate II was followed, making use of such data concerning dimensions of anode and cathode as could be gleaned from the published descriptions of Goodwin and Woehler's apparatus. (For key to drawing see page 15).

While a goodly number of trials with this apparatus were carried out, most of which were not over 2 to 3 hours duration, only 3 or 4 performed under different conditions will be described.

A run was made using pure  $\text{CaCl}$  of the very best grade, made by Baker & Adamson. The cylindrical, graphite vessel was filled with  $\text{CaCl}_2$  and then by the use of the auxillary electrode shown in the diagram an arc was struck with the inner surface of the anode container, and the  $\text{CaCl}_2$  gradually melted down in the vicinity of the arc until a small pool of fused  $\text{CaCl}_2$  was formed. The auxiliary electrode was now inserted directly into the fused  $\text{CaCl}_2$  and the current caused to flow through the bath directly. When sufficient electrolyte was melted the iron cathode R was



## PLATE II.

## Electrolyzing Apparatus No.1.

- A - Circular graphite anode.
- B - Metallic conductor connecting with bands on anode vessel.
- C - Soap-stone bottom for anode.
- C - Portland cement vessel.
- F - Space filled with asbestos-cement.
- R - Iron rod cathode (fastened to a stationery upright screw).

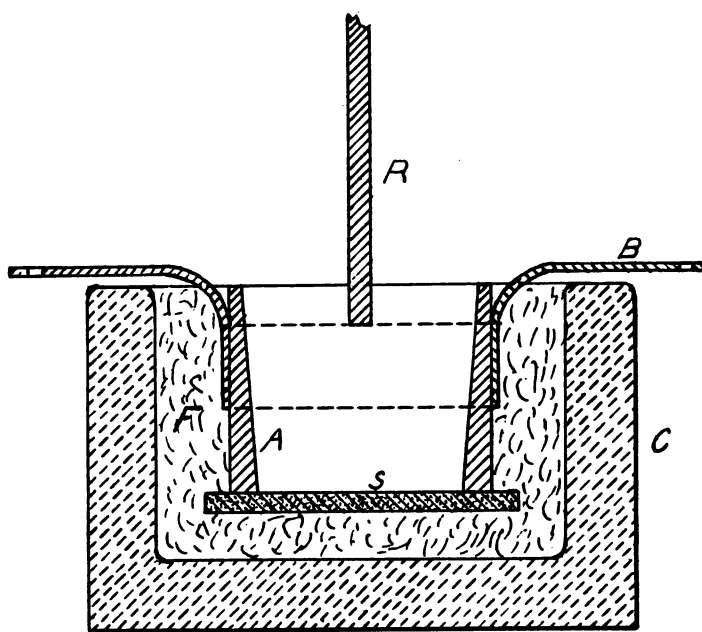
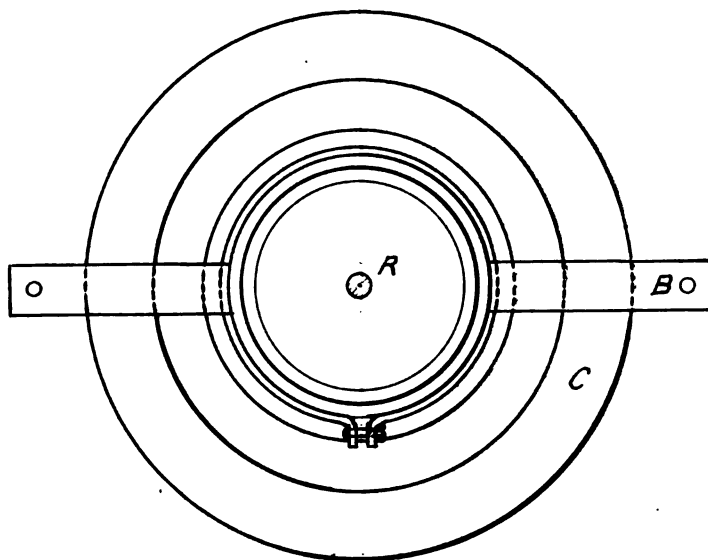
## PLATE III.

## Diagram No.1.

## Showing connection for apparatus No.1.

- C - Electrolyzing apparatus.
- R - Rheostat.
- A - Ammeter.
- V - Voltmeter.
- E - Auxiliary carbon electrode.
- S - Switch.
- D - Direct current dynamo.





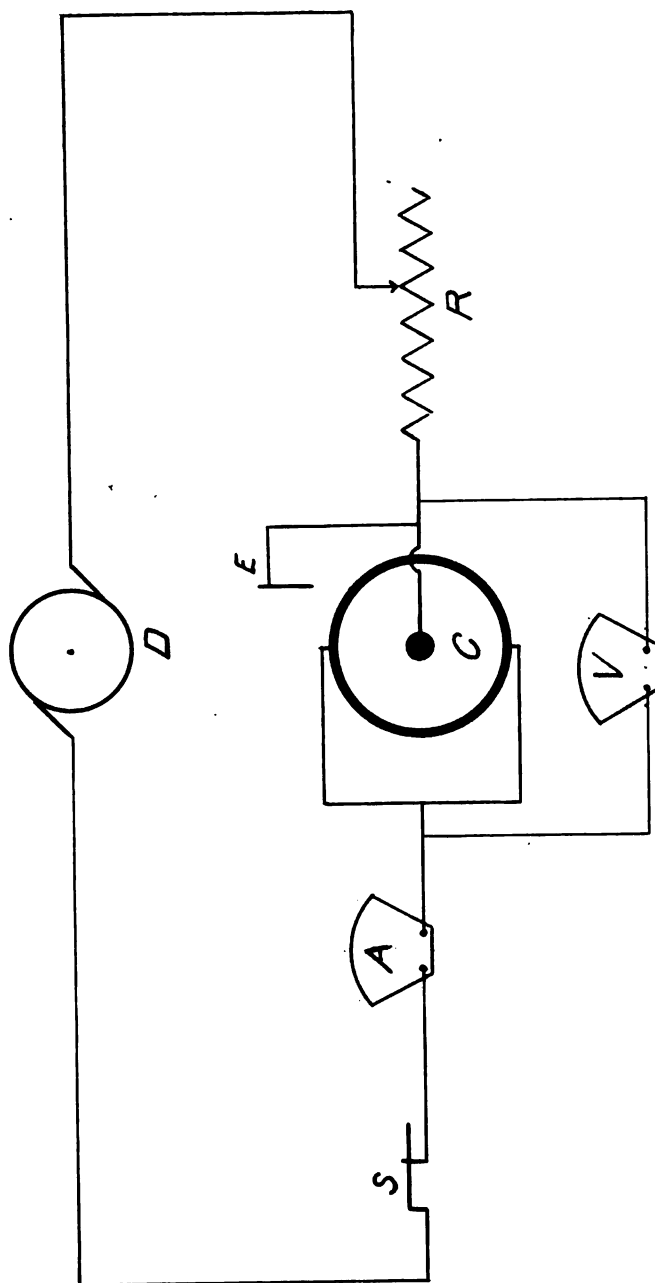
*Plate II*



lowered into the molten mass by means of the screw (R') and electrolysis begun. After a period of 3 or 4 minutes the odor of chlorine was noticed, and there was considerable cracking and snapping at the cathode and bursting forth of yellow flames. The current was gradually increased until finally the whole bath was in a state of fusion and 90 to 100 amperes were flowing. After waiting some minutes the iron cathode was cautiously raised from the bath but nothing was observed until an arc was struck between the end of the rod and the surface of the bath. The rod was again lowered and electrolysis continued for 15 to 20 minutes, at the end of which time bright beads of metallic calcium were noticed to coalesce around the iron rod and finally break away and swim around in the bath under the influence of the convection currents. It was immediately recognized that a furnace of the Borchert type was at hand so the current was gradually cut down as low as 40 to 50 amperes, (10 volts drop across cell) at which point a reguline deposit was noticed forming at the end of the rod. But it was now found impossible to keep all the bath fused next to the anode, and finally there was only a comparatively narrow channel of molten salt between anode and cathode. A glowing phenomenon, like a sheet of flame, was noticed at the anode. After the bath had been in operation under these conditions some time the iron rod was raised a trifle and electrolysis continued. The







*Diagram No. 1*

*Plate III*



calcium "rod" which was forming was very irregular in cross-section, and continued in spite of all efforts to "neck down" until the "rod" suddenly melted, causing an arc and interrupting of electrolysis. Part of the calcium formed was skimmed out before the bath solidified and the remainder gotten afterwards by loosening the solid  $\text{CaCl}_2$  from the walls of the anode vessel by immersion in  $\text{H}_2\text{O}$  and then breaking the solid chunk to pieces.

The fractured  $\text{CaCl}_2$  showed a very crystalline structure. It was also noticed in this bath, as well as in all others, that the current had passed through the bath comparatively near the surface and hence the bath was melted to only a shallow depth, while at the bottom of the anode containing vessel the bath had remained solidified and almost pure white, though the upper portion through which the current had passed for a long time during electrolysis was very dark colored. (See photograph, Plate 9)

Woehler used a mixture of 100 parts of  $\text{CaCl}_2$  and 17 parts of  $\text{CaF}_2$  by weight for his bath thus getting an electrolyte which fused at a much less temperature. Hence several trials were carried out in the apparatus described using such an electrolyte. The  $\text{CaCl}_2$  was from the same bottle as that used in the previous trials, while the  $\text{CaF}_2$  was ordinary powdered flourspar.

The two salts were intimately mixed together and then



fused down as previously described. After adjusting the current to 40 to 50 amperes it was noticed that a larger portion of the bath was kept in a fluid condition than when  $\text{CaCl}_2$  only was used as electrolyte. Again the melt seemed to be more liquid. Calcium was noticed to form quite rapidly at the cathode but not in a good, compact form. It grew out from the end of the iron rod in a very irregular manner, tending to extend across to the anode and short circuit the bath. Difficulty was experienced in getting a piece even an inch long on the iron cathode, an arc always being struck and melting all of the calcium off.

While no attempt will be made to discuss here the chemical phenomena of the baths tried, it may be well to point out the mechanical defects of the apparatus as viewed from an engineering standpoint.

1. The parts of the apparatus (anode container and cathode) are wrongly proportioned to to obtain proper cathode current density and still keep electrolyte in proper state of fusion.
2. The space intervening between anode and cathode is too small, allowing short circuits to occur.
3. The upper portion of the graphite anode vessel exposed to the air rapidly disintegrates, allowing carbon to fall into the bath.
4. When the bath solidifies the graphite anode container is cracked to pieces.



5. The metallic bands around the anode vessel become badly corroded causing poor contact.

#### EXPERIMENTS WITH APPARATUS NO.II.

In order to obviate some of the objections to the foregoing apparatus and at the same time have an apparatus practically the same capacity as Goodwin's, I designed the affair shown in Plate IV, the specifications for which are given on page 16 .

My chief aims in the design of this apparatus were as follows:-

1. To have an anode vessel with the same internal dimensions as Goodwin's apparatus.
2. An anode container which would not be cracked to pieces when the bath solidified and could be subjected to heavy currents and hard usage.
3. Large enough space between anode and cathode so that iron rods of various cross-section could be tried as cathodes.
4. An apparatus which would have as little radiating surface as possible.
5. To have the exposed portions of the graphite container protected from the atmosphere.

In almost all the trials with this apparatus the  $\text{CaCl}_2$  and  $\text{CaF}_2$  were in the proportions of 100 to 17 respectively. Some of the experiments were carried out with the pure so-called anhydrous  $\text{CaCl}_2$  which has hitherto been described,





while others were performed using crystalline  $\text{CaCl}_2$  which I first dehydrated. I shall first describe a run for calcium using the pure "anhydrous"  $\text{CaCl}_2$ .

A granulated carbon resistance furnace was first constructed and a weighed amount of  $\text{CaCl}_2$  placed in a Battersea clay crucible which sat in the carbon resistor. As the  $\text{CaCl}_2$  warmed up some steam came off and then a very little  $\text{HCl}$ . The whole mass then came to a state of quiet fusion at a very slight cherry-red color. Approximately the requisite amount of  $\text{CaF}_2$  was now slowly added and its action in the bath observed. The  $\text{CaF}_2$  seemed to gradually and easily dissolve in the bath. At the same time the bath as a whole grew more and more fluid and limpid. When all of the  $\text{CaF}_2$  had been added the bath seemed to have a cloudy appearance, some portions being rather transparent, while light yellow clouds floated about in other portions. After agitation and maintenance of bath in fused condition for some time it became fairly homogeneous and opaque in appearance.



## PLATE IV.

## Electrolyzing Apparatus No.2.

- A - Graphite anode built up of six sections, and held together by bolts in corners.
- W - Wooden case.
- F - Intermediate space packed with asbestos cement.
- S - Loose soap-stone bottom.
- S'--Soap-stone bottom bolted fast to anode.
- L - Carbon legs.
- C - Iron Cathode.(Fastened to stationery upright screw).
- B - Copper conductors leading to iron covering, I, which is held down on the top of anode by the corner bolts.

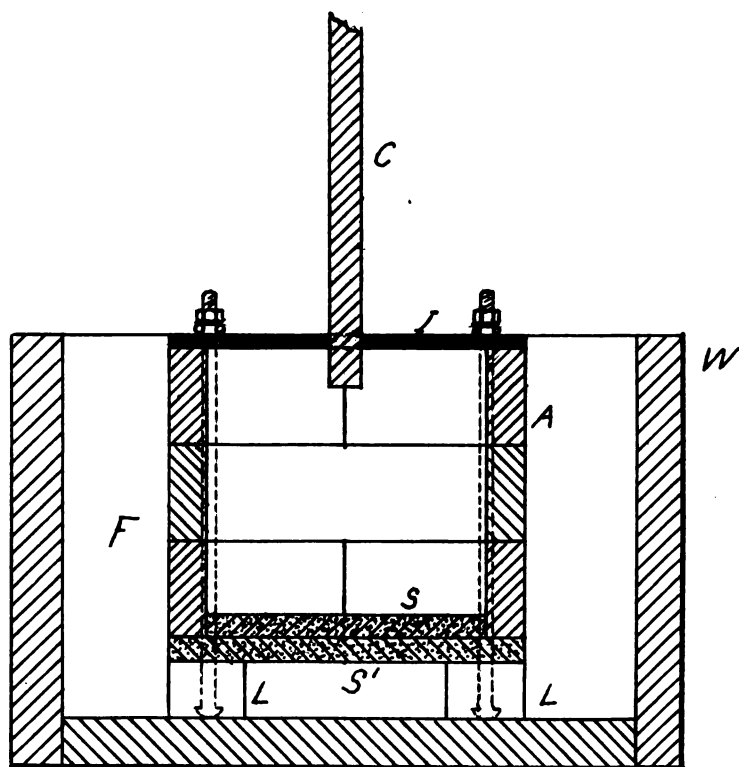
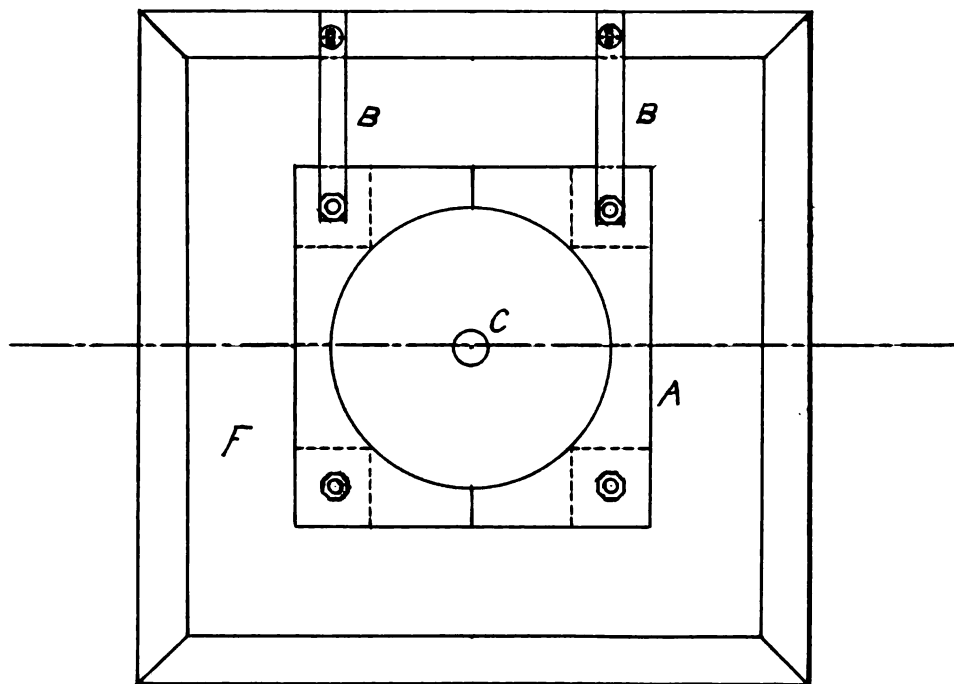
## PLATE V.

## Diagram No.2.

## Showing Connections for Apparatus No's. 2 &amp; 3.

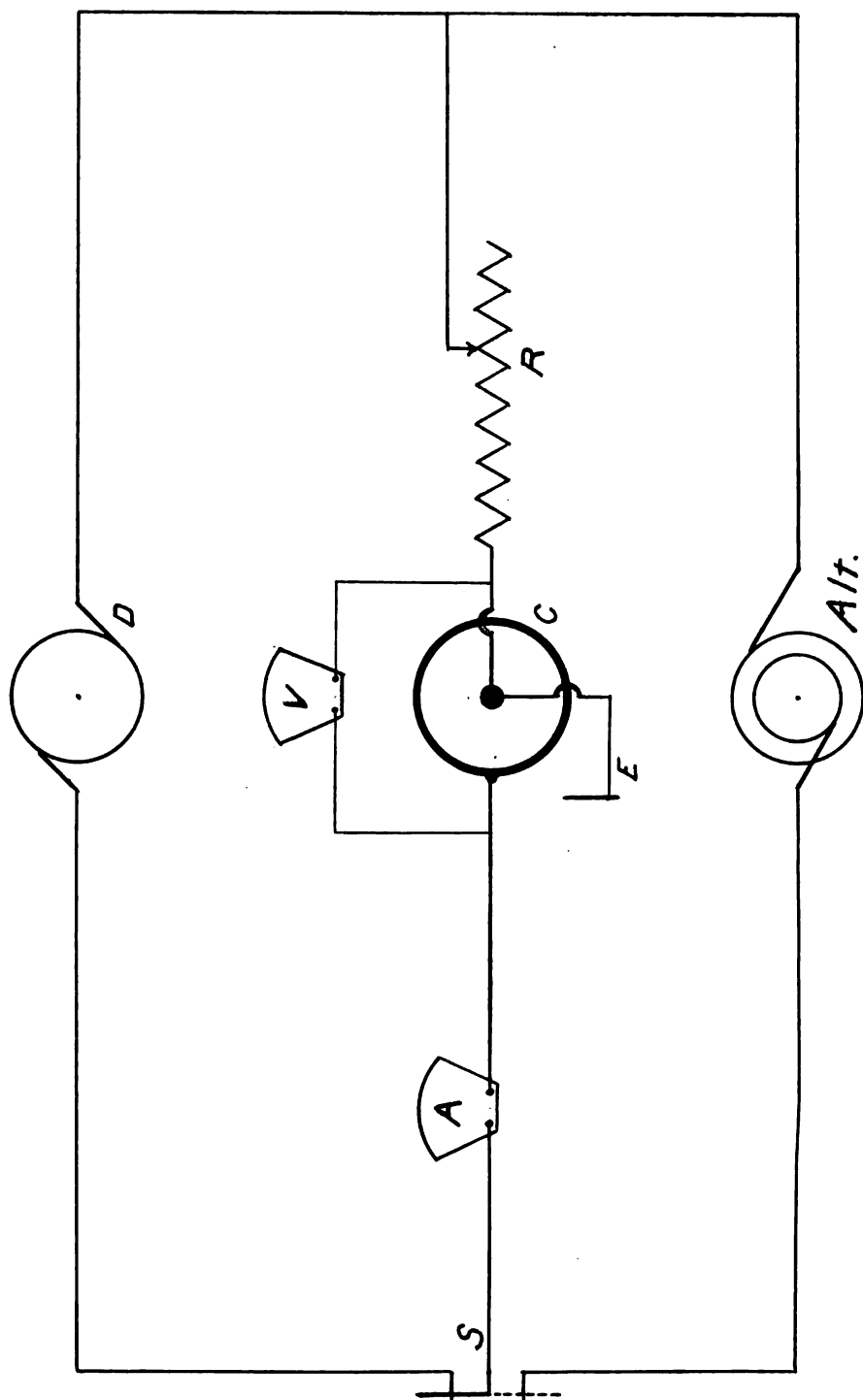
- C - Electrolyzing vessel.
- E - Auxiliary electrode.
- V - Voltmeter.
- A - Ammeter.
- S - Switch.
- R - Rheostat.
- D - Direct current dynamo.
- Alt.- Alternator





*Plate IV*





*Plate V* *Diagram No. II*





From the Battersea crucible the fused mass was poured into the anode vessel of the electrolyzing apparatus. An alternating current was now passed through the bath using a carbon rod an inch in diameter as the second electrode. A sufficient current to keep the electrolyte in a well fused condition was found to be almost 200 amperes. The electrolyte has a sort of swirling motion. At the surface of contact of large electrode with electrolyte all was quiet excepting perhaps now and then just a faint glow. The small electrode, however, was completely enshrouded with first a glowing sheet of flames and outside of this a circle of yellow flames bursting from the surface of the bath. In the space intervening the electrodes only now and then appeared a small yellow flame.

The alternating current was now switched off and the direct current switched on after first replacing the small electrode with an iron  $3/8$  inch in diameter. Chlorine was immediately detected coming off, and after some time calcium was noticed at the cathode, but it was soon in a molten condition and had to be skimmed from the bath. The current was gradually cut down to 75 or 80 amperes before calcium would adhere to the end of the rod in a reguline condition. With this current, however, only about  $1/4$  to  $1/3$  of the bath was fused. A sort of irregular mass of metallic calcium plus adhering  $\text{CaCl}_2$  was built out from the end of the rod, after an hour's run, as is shown in photographs.



The presence of water in the  $\text{CaCl}_2$  has an important influence upon the results attained, and in view of this fact several runs were tried using  $\text{CaCl}_2$  which had been subjected to dehydration as follows:-  $\text{Ca} \cdot \text{Cl}_2$  loaded down with water of crystallization was placed in the Battersea crucible of the electric resistance furnace afore described, and gradually "boiled down". When the mass had reached a pasty condition, a considerable volume of  $\text{HCl}$  came off, and then it soon began to melt down into a cherry-red. pasty fluid. Small bubbles of gas were noticed rising to the surface, exploding with a loud report and bursting in a yellowish flame sometimes tinged with a bluish color.

All of the electrolyte was next poured into the electrolyzing apparatus and subjected to a much higher temperature by passing an alternating current of about 200 amperes. A profusion of yellow flames was noticed bursting forth from around the small electrode and the whole surface of the electrolyte became covered with large transparent bubbles, of even an inch radius, of gas (hydrogen) which burst into highly colored flames with a loud report. If the heating be continued these transparent bubbles almost entirely disappear after a time, but no matter how long we continue to heat the electrolyte (or electrolyse) we never get rid of the small yellow flames around the smaller electrode. (cathode if electrolyzing).

Now there are two conditions under which we may electro-



lyse the above mentioned electrolyte: (a) Electrolyse after all of the gas bubbles (excepting those giving yellow flames) disappear; or (b) electrolyse before the formation of bubbles ceases.

In the first case chlorine is noticed coming immediately after switching on the direct current. Metallic calcium also appears at the cathode and comes out regularly, if proper conditions of temperature and current are maintained.

On the other hand, if we attempt to electrolyse before the  $\text{CaCl}_2$  is as thoroughly "dehydrated" as possible, that is, before the cessation of gas formation, we get entirely different results. If the bath has been heated little previously we get almost no chlorine given off at the anode, while at the cathode nothing is deposited if the temperature and cathode current density are high, and if within proper limits, a black, crispy mass resembling charcoal in appearance, and having seemingly good electrical conductivity is formed. By long continued electrolysis one may succeed in finally getting a poor reguline deposit, but the bath acts very capricious at all times.

In a preceding paragraph was set forth the chief aims in the design of apparatus No2 with which the above experiments were performed. These experiments have shown the apparatus to fulfill most of the requirements, but be-



fore proceeding with the chief objections to this general type of apparatus (Rathenau principle) for use either as a commercial apparatus or for carrying on research work, it is first desirable to give some facts concerning the physical nature of the deposit of calcium and the manner in which it forms reguline.

Of course it will be assumed that the electrolyte is in good working condition chemically and otherwise, all conditions being such as to contribute to the best formation of metallic calcium. My experiments have shown that whether the metal comes out with a coarse crystalline structure, (as it usually does) or in a compact, dense form, the deposit cannot form to any great thickness before becoming nodular on the surface, or even growing out in arborescent forms.

From analogy with the nature of deposits from aqueous solution (and also because of the particular design of apparatus used), the above results might be anticipated. In the refining of metals from aqueous solutions by electrolysis it has been found practically impossible to obtain a smooth deposit deeper than 1-2/2 inch, and in most cases the deposit becomes very nodular and uneven by the time the deposit is 1/2 inch thick.

There is no reason to believe that a reguline deposit from  $\text{CaCl}_2$ , or any other fused electrolyte should come out





in a smooth compact form for a practically indefinite thickness than there is in an aqueous solution. A glance at photograph (10) of a calcium deposit which has been sawed through will show that these formations have a core of fairly solid metallic calcium. This core is particularly solid near the base of the iron rod, but as we leave the center of this core and approach the outside of the formation we find the metal becoming more and more irregular and mixed mechanically with more or less  $\text{CaCl}_2$ . Still farther from the center of the core the metallic calcium and  $\text{CaCl}_2$  are hopelessly mixed together. (This fact has an important bearing upon the values obtained for current efficiency as will be shown later. ) To be sure, an irregular cathode deposit of considerable length can be formed but there is a greater waste of calcium and  $\text{CaCl}_2$  and hence lower and lower efficiency as the "rod" grows longer, on account of the increased mixing of the electrolyte with the metallic calcium formed. It must be born in mind that a piece of this deposit, consisting of metallic calcium and  $\text{CaCl}_2$  so intimately mixed mechanically as to appear almost homogeneous, is still a very good conductor of the electric current and hence may act as a cathode surface for a further deposit of metallic calcium, or a mixture as described, so that a stick of "metallic calcium" such as this is easily obtained.



Again, as intimated above, the particular design of electrolyzing apparatus used is such as to cause the formation of a more or less irregular calcium deposit. When we pass an electric current through this apparatus the current will seek that path which offers the least resistance, and of course we find the lines of current flow as near the surface of the electrolyte as possible. Indeed, as a consequence the bath remains comparatively shallow in spite of a considerable increase of current. Now then we do not put the end of an iron rod into the electrolyte to act as cathode without exposing a small portion of the side of the rod, as well as the bottom, to the electrolyte. Consequently more current will enter the edge, or side, of the rod, and hence a tendency for more calcium to deposit around the edge of the rod than directly on the flat end.

Cathode current density has been found to have an important effect upon the structure and nature of the deposit and hence upon current efficiency also. And it is a great objection to this "calcium rod" idea that nothing definite concerning the effects of current density can be determined, because, as the deposit grows the actual cathode surface is continually changing. However, since the current density is continually changing, the conditions under which a reguline deposit is formed are continually changed.

In regard to the use of iron rods of different diameters as starting cathodes, it may be stated that with the appa-



atus in hand it was found that if a rod much less than  $3/8$  inch in diameter was used the current density and hence the heating effect was so great that calcium would not form in the solid condition, while if a much larger rod were used the deposit was very crystalline and irregular and mixed with  $\text{CaCl}_2$  even near the base of the iron rod.

### EXPERIMENTS WITH APPARATUS NO.3.

Before taking up the question of current efficiency and in view of the inherent faults in the design of the apparatus used up to this time, I shall describe an electrolyzing apparatus of my own design in which I have endeavored to overcome some of the difficulties.

In the design of this apparatus I have endeavored to attain the following:

1. An apparatus in which the anode and cathode surfaces shall be definite under all conditions.
2. To be able to vary the current density and note the effects upon the electrolysis.
3. To accomplish the removal of the deposit of calcium as fast as formed without interfering with the uniformity of conditions.
4. Construction such that it would stand many "runs".
5. To confine the current to a definite amount of electrolyte, and to an invariable course through the same.

(For specifications of apparatus see page 25).



As in the preceeding experiments 100 parts of  $\text{CaCl}_2$  and 17 parts  $\text{CaF}_2$  were fused down in a Battersea crucible by means of a resistance furnace and after being thoroughly mixed was poured into the apparatus. Here, after first being thoroughly heated for some time with an alternating current (a carbon block was attached to the ribbon cathode in the opening (H) the direct current was switched on and electrolysis started. As the metallic calcium deposited to a sufficient thickness the iron ribbon was gradually raised, presenting new cathode surface.

Paul Woehler states that in his experience electrolyzing  $\text{CaCl}_2$  and  $\text{CaF}_2$  by the Rathenau method that a cathode current density of from 45 to 250 amperes per square centimeter can be used and a stick of calcium obtained. He based his figures upon the fact that the amount of current flowing through his apparatus was constant but the cross-section of the calcium stick varied at different parts. This is obviously a wrong basis upon which to come to such a conclusion, however. Nevertheless, my apparatus as first constructed had a cathode surface of such size that when sufficient current flowed to cause the whole bath to be in a well fused condition, there was a density of 45 to 50 amperes per square centimeter. The first two trials, however, proved that even this cathode current density is altogether too high, for the calcium would not deposit on





## PLATE VI.

## Electrolyzing Apparatus No. 3.

- C - Portland cement casing.
- N - Soap-stone end.
- S - Soap-stone bottom.
- W - Soap-stone sides.
- M - Soap-stone base for anode.
- A - Graphite anode .
- H - Aperture in soap-stone end N.
- R - Iron ribbon as cathode, to slide between soap-stone end N and iron block C.
- B - Copper conductor fastened to iron block C.

Connections for apparatus same as for apparatus No.2.



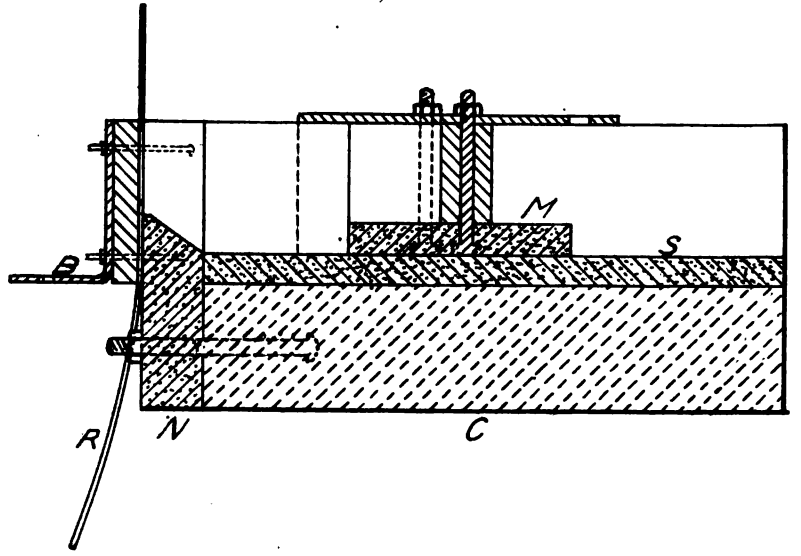
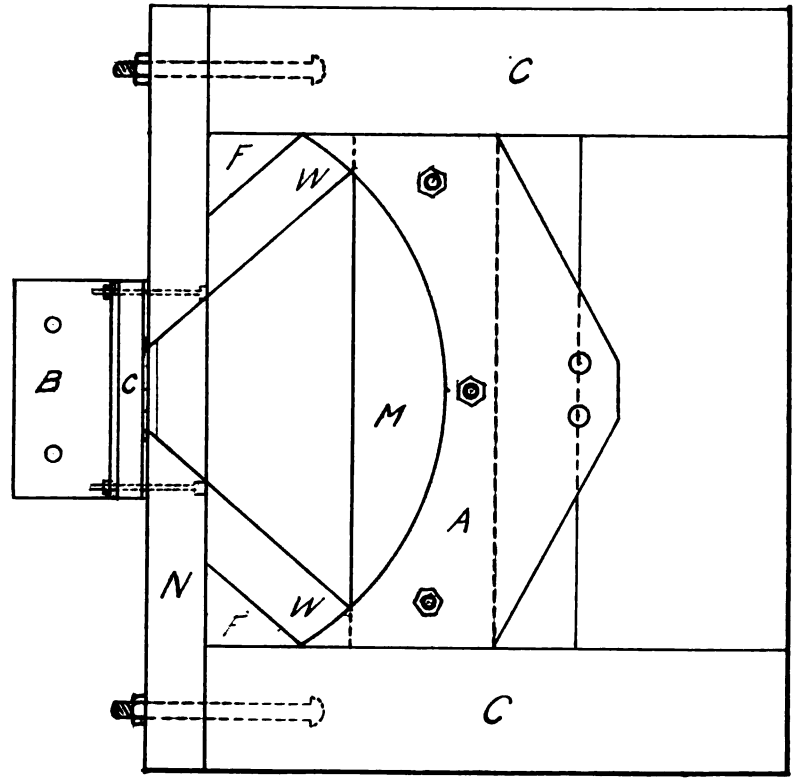
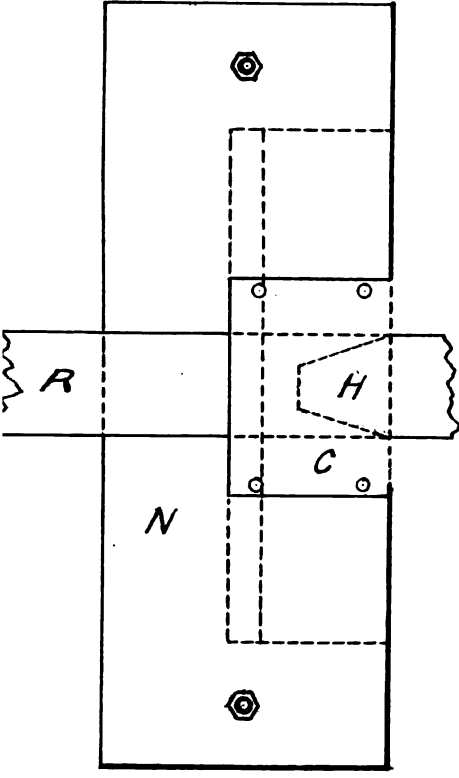


Plate VI  
Apparatus No. III



the iron ribbon, but simply melted and floated about in the bath.

The cathode opening (A) was then made larger and other runs made. A run made when the electrolyte was in good condition showed that calcium came out in the best physical condition at 10.6 amperes per square centimeter. (See photograph 11'). To be sure calcium will come out at a considerably higher current density, but under the particular set of conditions under which these experiments were performed the above current density was found to give the best results. At a lower current density the calcium carries up more  $\text{CaCl}_2$  with it which tends to solidify just above the surface of the bath and cause the iron ribbon to be cemented fast.

As will be seen from the photograph, if the calcium does not sufficiently alloy with the iron the two will break apart upon cooling some distance above the bath on account of difference in rates of contraction of the two metals. When the calcium does alloy with the iron ribbon the latter expands at these places, giving rise to little "hills" in the ribbon. Examination of the iron at these points after removal of the calcium show it to be softer.

Anode current density is not of so great importance as is cathode current density. We simply need sufficient anode surface over which the  $\text{CaCl}_2$  bath can fuse as far as it likes with the given current in use. If the anode density is un-



duly great, arcing or glowing phenomon takes place at the junction of the carbon and fused bath increasing the total resistance offered by the cell .

#### CURRENT EFFICIENCY.

While the current efficiency at which calcium can be reduced from its chloride is of great importance from an engineering standpoint, yet if the exact conditions under which such efficiency is obtained can be maintained are not known, the figures have lost much of their value. Still, although we do not understnad fully the nature of the process, to know what efficiency can be attained at times is interesting and encouraging.

Both Goodwin and Woehler made current efficiency determinations, and not only their results but also their methods of determining them were very different. Goodwin determined the current efficiency for a run of several hours duration using only  $\text{CaCl}_2$  as electrolyte. He separated the metallic calcium from the  $\text{CaCl}_2$  by pounding loose the encasing  $\text{CaCl}_2$  which had solidified about the "rod" of calcium. The calcium thus mechanically separated was weighed and the efficiency figured. His highest efficiency was 40%.

On the other hand Woehler, who electrolyzed 100 parts of  $\text{CaCl}_2$  and 17 parts of  $\text{CaF}_2$ , made a mark on the forming calcium rod at the level of the bath, electrolyzed five minutes (gradually raising the rod) and made another mark





at the level of the bath. This section was cut out after the run, and dissolved in a weak acid solution, the hydrogen collected and from this the amount of calcium computed. He claims an efficiency of 82.2%. While Woehler would naturally obtain a higher current efficiency than Goodwin by employing a mixed electrolyte yet the method of Woehler is open to criticism.

Goodwin's method gives us the efficiency for the actually available metallic calcium, while Woehler's efficiencies are too large because; from my description of the nature of the deposited calcium, much of the metal was in a non-available form;- that is, so intimately mixed with  $\text{CaCl}_2$  that it would be almost impossible to separate it mechanically or otherwise.

The method which I used in determining current efficiency was that of Goodwin, but I had to be very careful to completely break up the deposit in order to be sure that all of the  $\text{CaCl}_2$  was eliminated, for the specific gravity of the latter is so much higher than that of the metal as to very appreciably raise the apparent efficiency. Some of the pieces were even boiled in alcohol (anhydrous) in order to facilitate the removal of the  $\text{CaCl}_2$ .

The following four results, the best obtained, are submitted, all of which are for baths of 100 parts pure  $\text{CaCl}_2$  and 17 parts  $\text{CaF}_2$ .



## APPARATUS NO. 2.

No. 1. Current 76.4 amperes, Time 70 minutes, Current Efficiency 67.65%.

No. 2. Current 51.5 amperes, Time 57 minutes, Current Efficiency 75.6%.

## APPARATUS NO. 3.

No. 1. Current 45 amperes, Time 12 minutes, Current Efficiency 84.6%.

No. 2. Current 70 amperes, Time 10 minutes, Current Efficiency 96.3%.



## CHEMICAL CHANGES IN ELECTROLYTE.

On page 18 was described the action of the bath during electrolysis both when water was present and when the bath had been previously been 'dehydrated.' If the bath had been thoroughly heated for some time previous to the passage of the direct current, calcium was formed quite readily, other conditions being favorable. Now it will be remembered that the dehydration proceeded with the following successive results after the application of the heat to the  $\text{CaCl}_2 + \text{H}_2\text{O}$ :- Firstly, steam came off; secondly,  $\text{HCl}$  fumes, then bubbles of hydrogen appeared all over the bath and lastly only the yellow flames remained. As stated before, these yellow flames were never gotten rid of entirely under any conditions. They exist only in the very hottest part of the bath, i.e. at the cathode if direct current is used, and if alternating current is used only at the smaller electrode. For the most part they appear to be burning hydrogen, but no doubt some other substances are present also.

In view of the fact that it is almost impossible to get such data as would give an exact insight into the chemical composition of the bath, I can give only my belief as to what actually occurs. And in this I am influenced by the views of Woehler who has made similar observations. Woehler claims that after the temperature of the bath has reached



a certain value the  $\text{H}_2\text{O}$  which still remains begins to combine with the  $\text{CaCl}_2$  according to the following equation:-  
 $\text{CaCl}_2 + \text{H}_2\text{O} = \text{Ca} \begin{smallmatrix} -\text{OH} \\ -\text{Cl} \end{smallmatrix}$  . This compound releases water with difficulty, and furthermore during electrolysis would probably react with the metallic calcium to form anhydrous oxychloride and hydrogen. This theory, while worthy of close consideration, does not explain why hydrogen bubbles and the yellow flames come off during the heating with alternating current. Nevertheless, the above equation probably states the condition of affairs some-where nearly right. So far as the whole truth is concerned we need much more data of a kind which is very difficult to get.

It is a well known fact that if in the electrolysis of  $\text{NaCl}$ , the temperature of the electrolyte becomes too high the sodium will redissolve in the electrolyte to form a hypothetical subchloride, and but little sodium will be obtained no matter how high the current density may be.

Such an assumption has been made by some regarding the electrolysis of  $\text{CaCl}_2$ :-  $\text{CaCl}_2 + \text{Ca} = 2 \text{CaCl}$ .

Richard Lorenz has shown that lead and zinc will dissolve in their respective chlorides if the temperature is raised to a certain value. The three factors upon which the phenomenon depends are given as follows: "Temperature of bath, volatility of the metal, and its solubility in the bath."

He farther states that this "metalnebel", metallic cloud, as he terms the dissolved metal, may be either (a) a real





solution of the metal in its fused haloid salt, or; (b) a mere pulverization of it in suspension. He prefers the former view.

I have called attention to the fact that those portions of the bath through which a direct current had passed for a considerable time were colored black.

A piece of this black  $\text{CaCl}_2$  was found to decompose water, liberating hydrogen and forming a white precipitate of  $\text{Ca}(\text{OH})_2$  suspended in a clear solution, but leaving no black residue. This showed that the coloration of the  $\text{CaCl}_2$  was not due to the disintegrated carbon but to either finely divided metallic calcium or the subchloride.

Since  $\text{CaCl}_2$  is soluble in alcohol (anhydrous) and metallic calcium is not, a piece of the solidified electrolyte was placed in this solvent with the result that the  $\text{CaCl}_2$  was dissolved and a finely divided deposit formed at the bottom of the test-tube. The alcohol was poured off and some water then poured on the precipitate. Hydrogen immediately began coming off quite briskly. A drop of  $\text{H}_2\text{SO}_4$  was next added to the solution and instantly the whole black precipitate was changed to snow white  $\text{CaSO}_4$ , and the heat developed from the reaction was sufficient to cause the ignition of the hydrogen liberated.

The two experiments just described do not prove absolutely that the dark particles are metallic calcium instead of  $\text{CaCl}$ ; but from the physical qualities, as metallic



appearance and specific gravity observed, it was concluded that these particles must exist as finely divided calcium mechanically suspended in the bath when the latter is solidified.

Now from analogy it is very likely that calcium dissolves to some extent in  $\text{CaCl}_2$  at a high temperature the same as lead or zinc have been found by Lorenz to dissolve in their respective chlorides. However there are grounds to believe that the solution of calcium in  $\text{CaCl}_2$  ought to be regarded as taking place in a manner exactly parallel to the solution of  $\text{CaCl}_2$  in  $\text{H}_2\text{O}$ , rather than to assume that a subchloride is formed. As such a compound has never been formed under any conditions by anyone so as to be recognized as a definite chemical compound, surely there is no reason to state without any qualifications that such a compound is formed in the electrolysis of  $\text{CaCl}_2$ . If we assume that the calcium is really soluble in the  $\text{CaCl}_2$  while the latter is at a high temperature as stated, we can also naturally infer that as the  $\text{CaCl}_2$  cools down that the solubility of the calcium in  $\text{CaCl}_2$  decreases and hence crystallizes out as it were.

In discussing the effects of dissolved metallic zinc or lead in their respective chloride baths which are undergoing electrolysis, Lorenz states that the metal acts as a depolarizer, and farther, that no metal will be deposited at the cath-



ode until the bath has become saturated with the metal.

To be sure there is some depolarization occasioned in the case of calcium also, but whatever may be the state of affairs for Zinc and Lead, it is certain that Ca can be deposited from a  $\text{CaCl}_2$  bath before it is saturated with the metal. This fact was proved while obtaining the decomposition voltage curves which follow. The electrodes used were two inches apart and placed in a  $\text{CaCl}_2$  bath which had never been electrolyzed before. There was much molten  $\text{CaCl}_2$  surrounding the electrodes and plenty of chance for circulation of electrolyte between electrodes. In several of these determinations of decomposition voltage easily recognizable deposits of calcium were obtained, although the current used was small and the duration of its passage only a few minutes at a time. Indeed that most of the curves have well defined "knees" in them is sufficient proof of the fact. Curve II was taken for a  $\text{CaCl}_2$  bath which had metallic calcium suspended in it from previous runs, and it will be noticed that there is no well defined "knee" in the curve. As stated in a preceeding paragraph the  $\text{CaCl}_2$  loaded down with metallic calcium possessed greater electrical conductivity in the cold state, and hence this fact might also have something to do with causing a gradual turn in the curve.



## DECOMPOSITION VOLTAGE CURVES.

As just intimated the study of the decomposition voltage curves which would be obtained under various conditions would throw much light on the best chemical composition of the bath as well as best physical conditions, correct temperature etc. at which the electrolysis ought to be carried on for most successful results. Although prevented by lack of time and the necessary pyrometer for determining temperatures, experiments along this line were not carried on as far as desirable. However, a few results have been obtained which are of at least some value.. On Plate VII is shown a diagram of the apparatus used, and on page 37 a description and data concerning same.

It must be born in mind that the value of the decomposition voltage for a fused salt will depend not only upon the chemical composition of the electrolyte and its temperature, but also upon the nature of the electrodes used and to a slight extent upon their geometrical disposition with respect to eachother.

In the experiments carried out a  $\text{CaCl}_2$  electrolyte only was used and in each case the data taken for the curve when the bath had just reached a nicely molten condition. (a bright cherry red).

Curve No. III was obtained with an anode of graphite and a cathode of polished sheet iron each 1 inch square and separated 1 inch. After the current had been passed





and the data obtained the electrodes were removed and examined. The anode, of course, was unchanged; while the cathode showed no deposit of Ca, or any calcium Fe alloy; it was appreciably corroded. By extending the resistance line we get 2.04 volts as the decomposition voltage.

Practically the same conditions were maintained in getting data for curve No.4 except for a slight increase of temperature as evidenced by the slope of the resistance line of the latter curve.

The critical voltage for this curve is about 2.76 volts. An examination of the cathode after the run showed it to be covered with a thin bright deposit of calcium which decomposed water. After the calcium was dissolved off the iron was left in a soft corroded condition. No doubt an alloy was formed with the iron at its surface.

As previously explained Curve No. 2 was obtained for a bath which had previously electrolyzed and contained much metallic calcium in the electrolyte. If we extend the very flat resistance line to the Y axis we obtain 2.62 volts as the decomposition value.

Curve No. V shows a very steep resistance line due to the fact that only the tip ends of the electrodes were immersed in the molten electrolyte. The electrolyte was pure  $\text{CaCl}_2$ . Extension of the resistance line shows a critical voltage of about 2.75.



## PLATE VII.

Details of Electrodes for Obtaining Decomposition o  
Voltage Curves.

A - Graphite anode.

C - Iron cathode.

H - Large hole through iron cathode.

S & S' - Soap-stone separators.

M - Binding screw.

B - Bolt for holding pieces together.

N - Bolts for holding iron cathode to support S'.

## PLATE VIII.

## Diagram No.3.

Showing disposition of Apparatus for Obtaining Decom-  
position voltage curves.

E - Electrodes in  $\text{CaCl}_2$  in Battersea crucible.

F - Liquid rheostat provided with three electrodes,

•<sub>1</sub> •<sub>2</sub> •<sub>3</sub>

S - Switch.

D - Direct current dynamo.

V - Low reading Weston voltmeter.

A<sub>1</sub> " " " ammeter.

T - Step-down transformer.

A - Ammeter.

S<sub>2</sub> - Switch.

Alt. Alternator.

R - Rheostat.







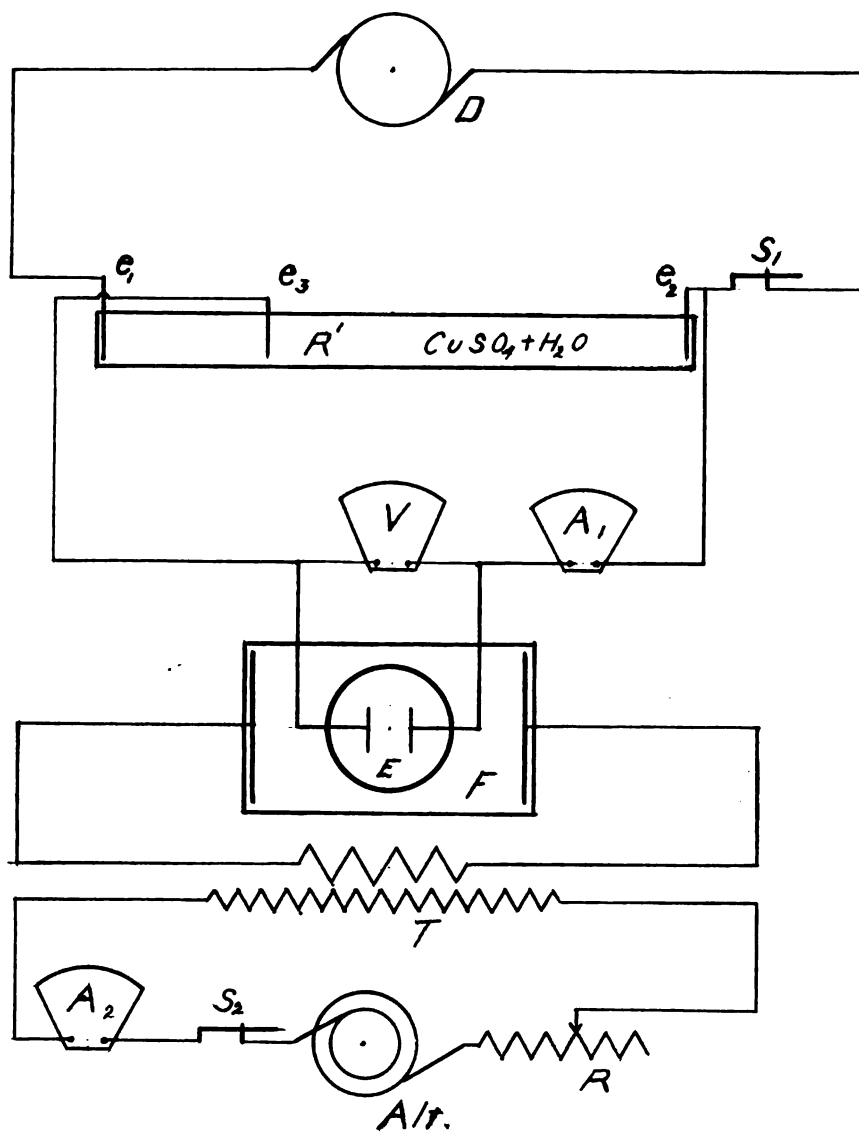


Plate VIII

Diagram No. III





A very low critical voltage of a pure  $\text{CaCl}_2$  electrolyte was obtained by employing iron for both anode and cathode. The electrodes were each one inch square as before, but separated two inches. A decomposition voltage of 1.425 was obtained. Inspection of the electrodes after the experiment showed the anode to be badly corroded and covered with iron chloride, while the cathode had a fine, smooth deposit of calcium on it.

All of the above values of decomposition voltage for  $\text{CaCl}_2$  are far below the theoretical value (3.727 for cold  $\text{CaCl}_2$ ). But this is no more than is to be expected when we remember that the ions liberated at the electrodes may have some affinity for them and form chemical compounds. The formation of the iron chloride in the ordinary chemical way is attended with the liberation of heat and consequently we would expect a lowering of the decomposition voltage, when using an iron anode, by an amount equivalent to the heat energy evolved in formation of iron chloride, since this compound is formed at the anode electrolytically.

Since in many of the experiments performed calcium seemed to possess the power of forming a superficial alloy with the iron cathode this fact may help to lower the critical voltage. If we could employ two electrodes which would be entirely inert toward the products of electrolysis and the electrolyte, we might reasonably expect to get results



agreeing fairly close with the theoretical value, if from this we also subtracted the voltage corresponding to the heat supplied to the  $\text{CaCl}_2$  to raise it from the ordinary temperature to the fusion point. This latter step is necessary since the heat of formation is given for solid  $\text{CaCl}_2$ .

However, the above values are probably approximately correct for electrodes of graphite and iron,- the two electrode materials which would be used in the electrolysis of  $\text{CaCl}_2$  on an industrial scale.

Another point which is of importance here is the fact that these data and results concerning decomposition voltage values entirely disprove the Bunsen theory concerning the idea that a high current density must be used, for the above data show that calcium was obtained at a current density as low as 1.7 amperes per square inch of cathode surface.

Indeed, calcium will simply appear at the cathode in an electrolyte of the proper chemical composition if the temperature is such as to bring the electrolyte into the proper state of fluidity and the current density is below a certain abnormal value.

In conclusion, I believe that in the study of the decomposition voltages of the fused  $\text{CaCl}_2$  I have only touched upon a field of investigation which would make a splendid theme by itself, and, if carried out carefully in detail would throw much light upon the best chemical composition



of electrolyte to be employed for the successful production of calcium.



## CONCLUSION.

A review of this thesis will show that the study of the production of calcium as herein carried on has been mostly of a qualitative nature. But it has of necessity been so, for on account of lack of understanding of the chemical conditions existing in the electrolyte the obtaining of calcium has been a matter of happening to strike proper conditions. Nevertheless, the phenomena exhibited when calcium was not obtained were studied as carefully as those shown when calcium was obtained.

In summarizing what has been accomplished in the prosecution of this thesis attention is called to the following points:-

1. Troubles arising from faulty design of apparatus have been pointed out.
2. Apparatus have been designed which help to obtain more definite data concerning proper conditions of electrolysis.
3. Definite data have been obtained concerning the proper cathode and anode current densities.
4. The physical structure of the calcium deposited under certain conditions has been described.
5. Current efficiencies are given.
6. Phenomena exhibited during dehydration of  $\text{CaCl}_2$  are described.





7. Evil effects resulting from presence of  $H_2O$  in the electrolyte during electrolysis are set forth.
8. The difference in the demeanor of  $CaCl_2$  and a  $CaCl_2$   $CaF_2$  bath is described.
9. The subchloride theory and experiments bearing thereon are discussed.

(a) It was found that calcium dissolves or disintegrates in  $CaCl_2$  at high temperatures the same as lead and zinc dissolve in their respective chlorides.

10. Proof is shown that calcium can be deposited from fused  $CaCl_2$  before the bath is saturated with metallic calcium.
11. Decomposition voltage curves have been obtained for fused  $CaCl_2$  under different conditions.
12. No evidence is found substantiating the Bunsen current density theory.

In conclusion it may be stated that although the design of the best type of electrolyzing apparatus is very essential for the successful production of calcium the obtaining of a proper electrolyte, which can easily be dehydrated and maintained under uniform conditions chemically, is of far greater importance for success in working out a commercial method. Since  $CaCl_2$  is one of the most hygroscopic salts known, and metallic calcium has a tremendous affinity for oxygen, it is very probable that to work out a commercial



process which can be run continuously under uniform conditions, some easily dehydrated salt or mixture of salts must be used as electrolyte.



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## DATA FOR DECOMPOSITION VOLTAGE CURVES.

Curve No . 1.

Both electrodes iron,  
one inch square and sep-  
arated two inches. Pure  
 $\text{CaCl}_2$  .

Curve No. 2.

Graphite anode one inch square.  
Iron cathode one inch square.  
Electrodes separated one inch.  
Bath of  $\text{CaCl}_2$  had previously  
been electrolyzed.

<u>Volts</u>	<u>Amperes</u>
--------------	----------------

1.00	1.10
1.40	1.35
1.70	1.50
1.85	1.65
1.80	1.70
1.90	1.90
2.00	2.15
2.05	2.35
2.10	2.60
2.20	3.00
2.20	3.25
2.40	3.80
2.70	4.90

<u>Volts</u>	<u>Amperes</u>	<u>Volts</u>	<u>Amperes</u>
--------------	----------------	--------------	----------------

0.433	0.05	2.300	1.30
0.560	0.10	2.330	1.40
0.600	0.10	2.330	1.50
0.717	0.10	2.434	1.60
0.966	0.20	2.535	1.75
1.233	0.35	2.567	1.91
1.466	0.50	2.567	2.00
1.734	0.60	2.567	2.15
1.834	0.80	2.660	2.55
2.067	0.95	2.660	2.80
2.167	1.20	2.660	3.20



## DATA FOR DECOMPOSITION VOLTAGE CURVES.

Curve No.3.

Graphite anode one inch square.  
 Iron cathode one inch square.  
 Electrodes separated one inch.  
 Pure  $\text{CaCl}_2$  electrolyte.

Curve No.4.

Graphite anode one inch square. Iron cathode one inch square. Electrodes one inch apart. Pure  $\text{CaCl}_2$  bath.

Volts Amperes      Volts Amperes.

0.10	0.025	2.7	1.3
0.40	0.10	2.7	1.35
0.65	0.15	2.725	1.55
0.95	0.25	2.95	1.95
1.1	0.45	3.15	2.35
1.5	0.80	3.30	2.75
1.75	0.85	3.40	3.20
1.85	1.05	3.70	3.90
2.2	1.10	3.80	3.95
2.6	1.20	4.10	4.30
2.7	1.25	4.20	4.50

Volts Amperes

0.95	0.10
1.25	0.25
2.00	0.60
2.70	0.60
3.00	0.90
3.00	1.00
3.05	1.15
3.05	1.40
3.25	2.20
3.30	3.4
3.75	4.15
3.90	5.00



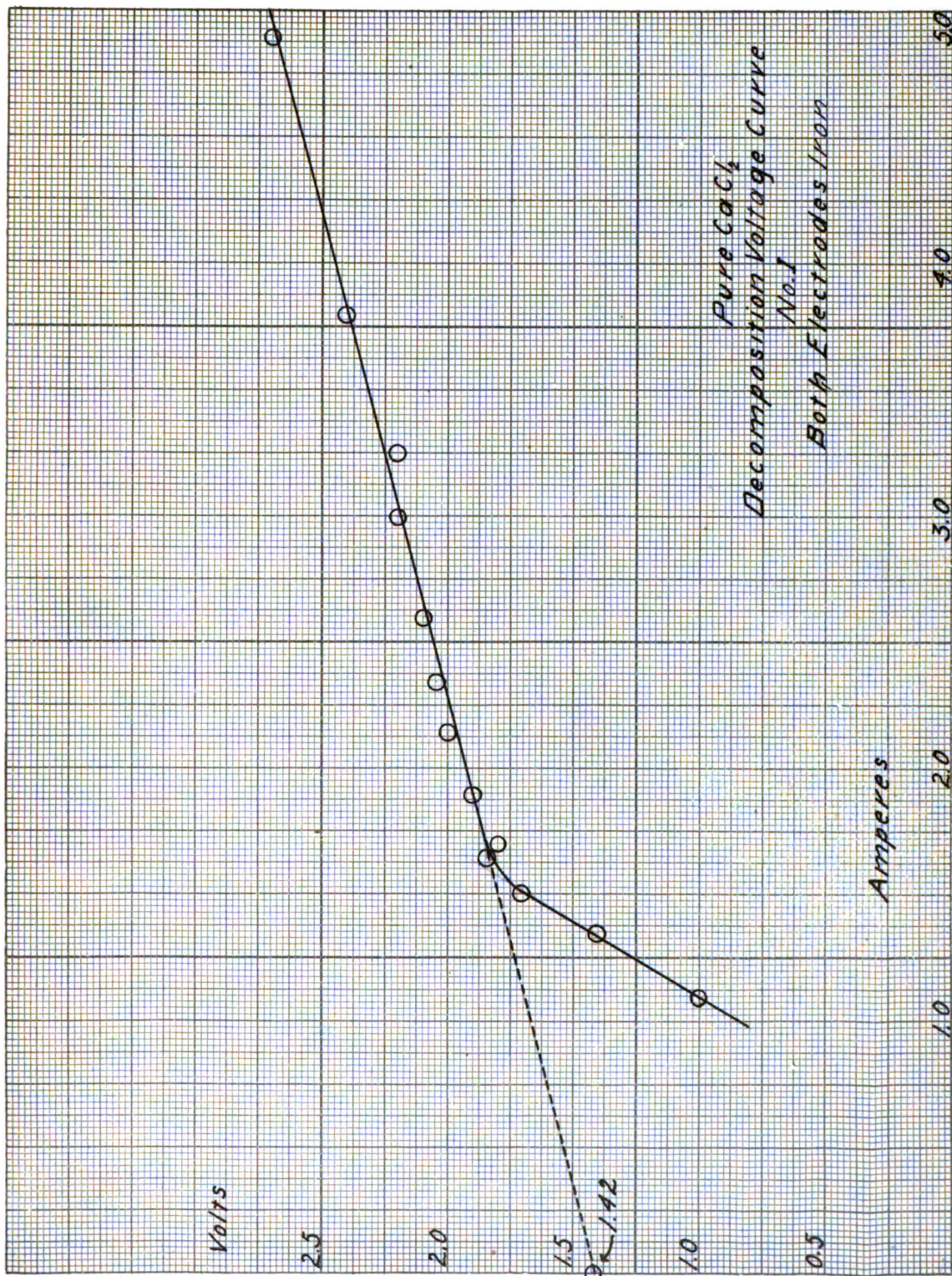
## DATA FOR DECOMPOSITION VOLTAGE CURVES.

Curve No. 5.

Graphite anode and iron cathode. Only tip ends immersed in pure  $\text{CaCl}_2$  bath. Electrodes one inch apart.

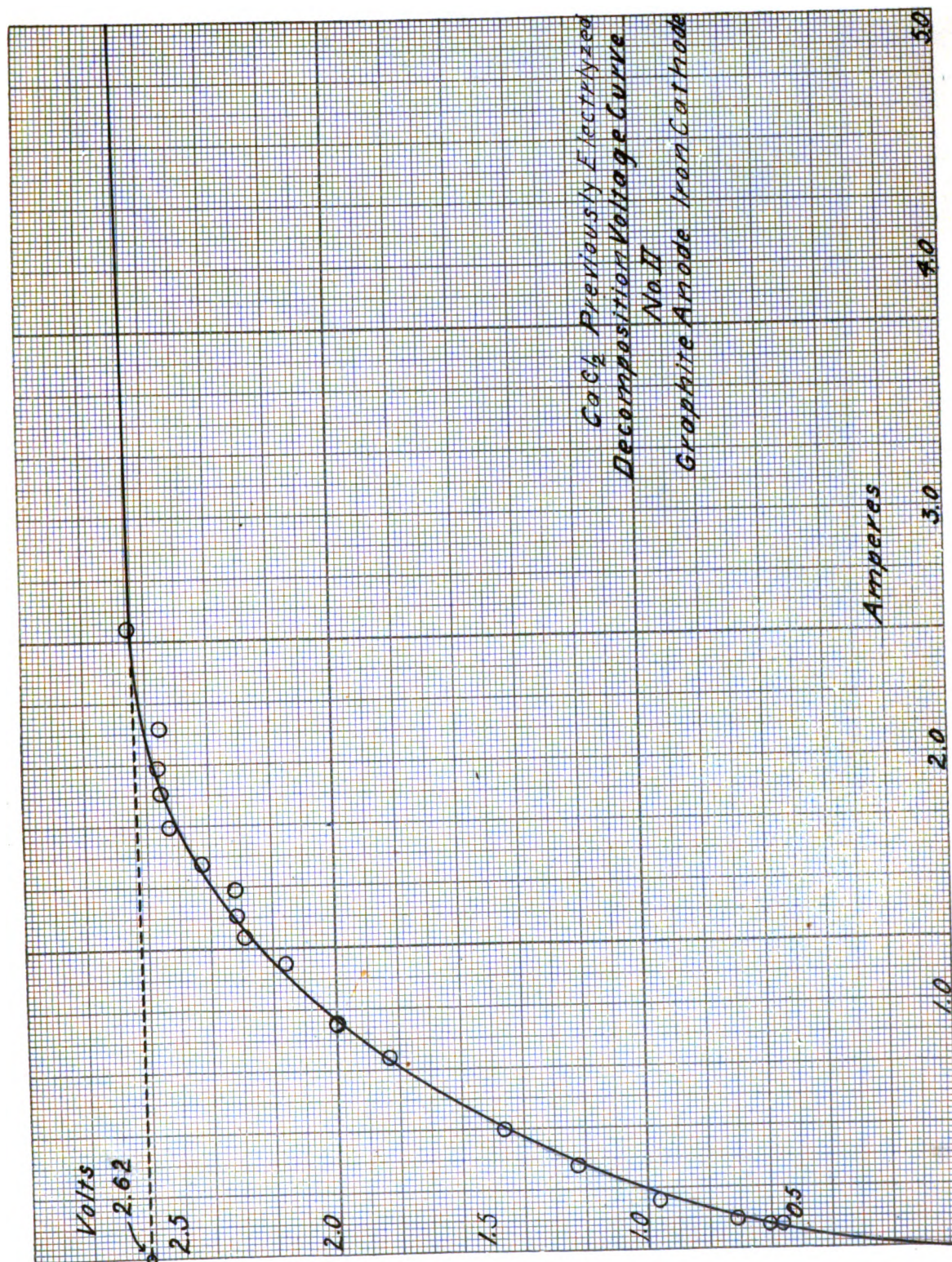
<u>Volts</u>	<u>Amperes</u>
0.30	0
0.44	0
0.55	0
0.70	0.025
0.81	0.03
1.05	0.03
1.10	0.03
1.45	0.04
1.755	0.04
2.15	0.05
2.45	0.05
2.75	0.06
2.90	0.10
3.10	0.13
3.25	0.20
3.50	0.24
3.65	0.35





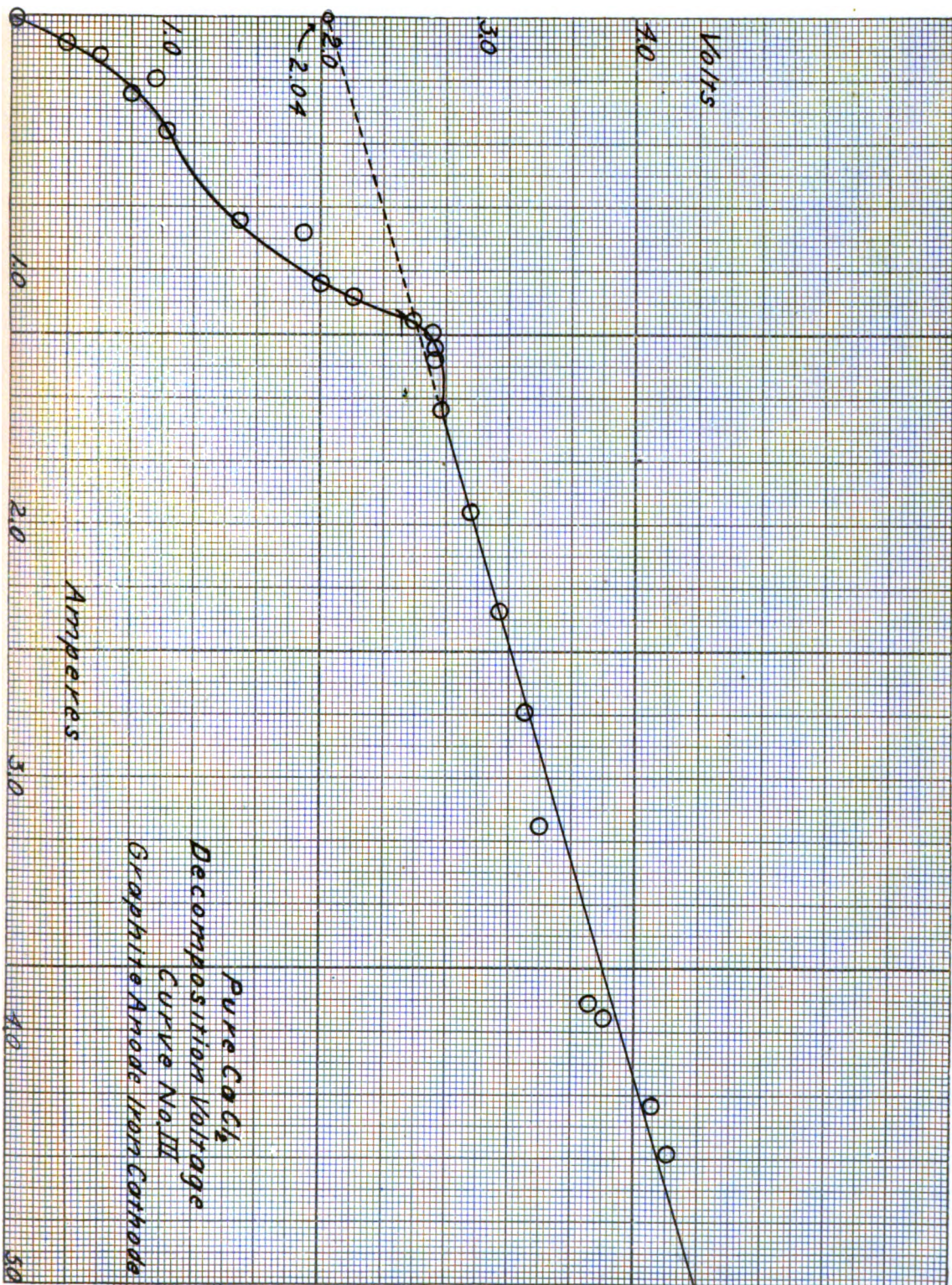






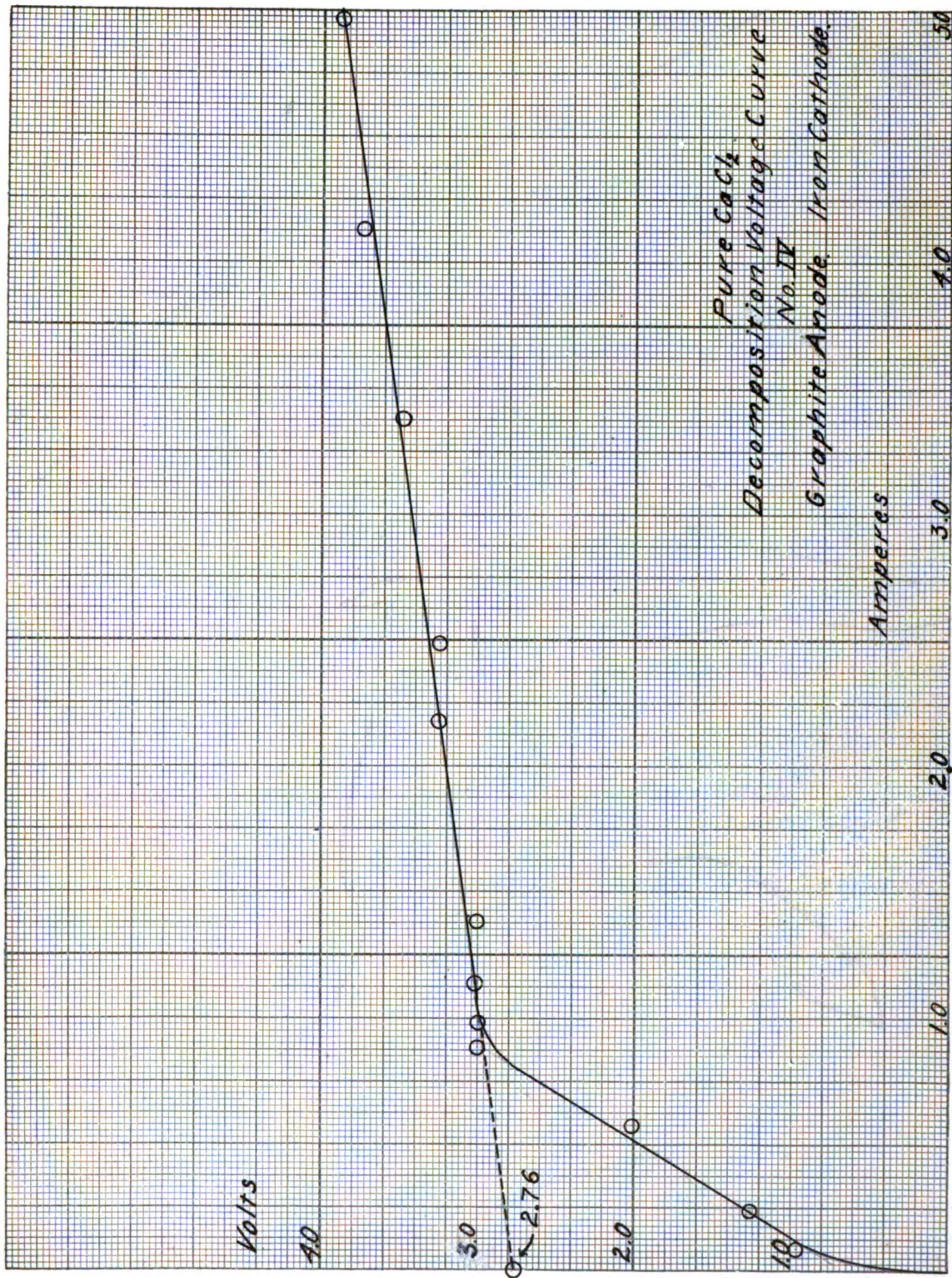






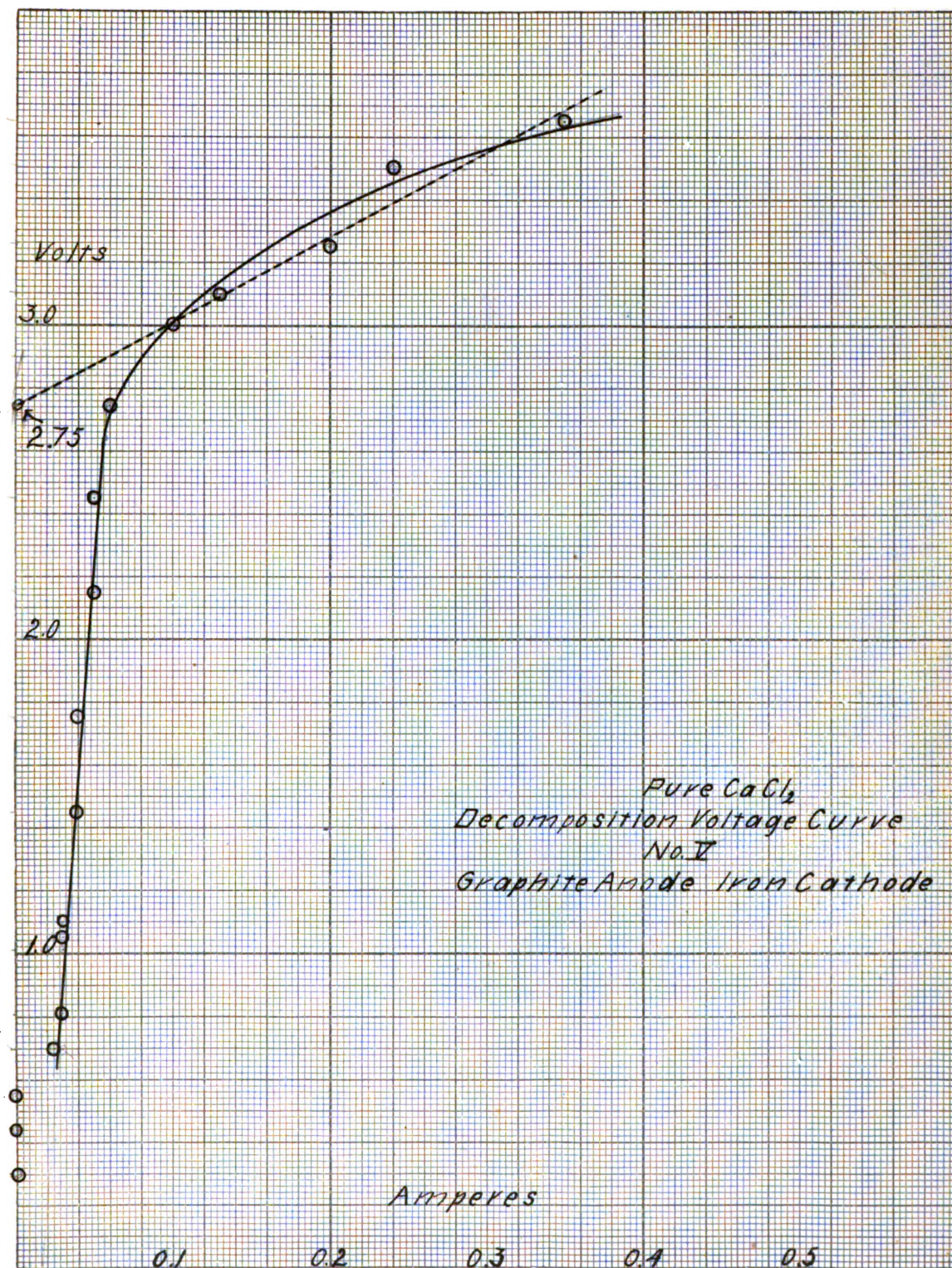






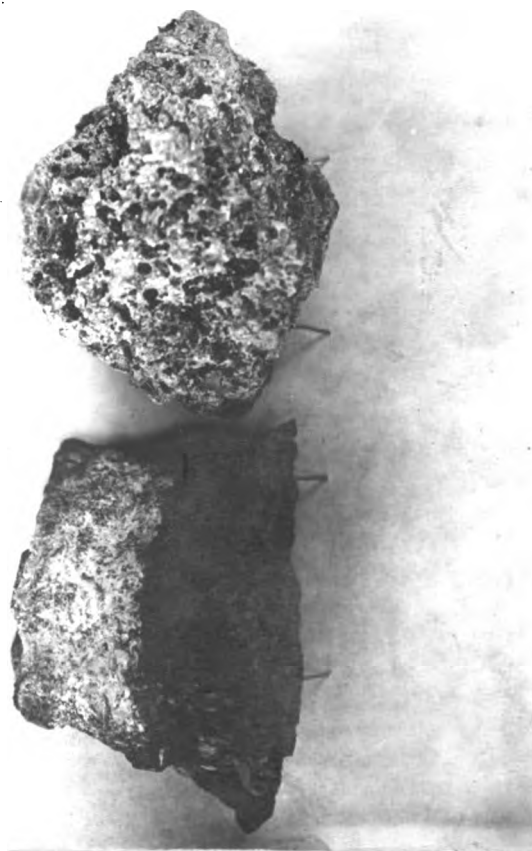






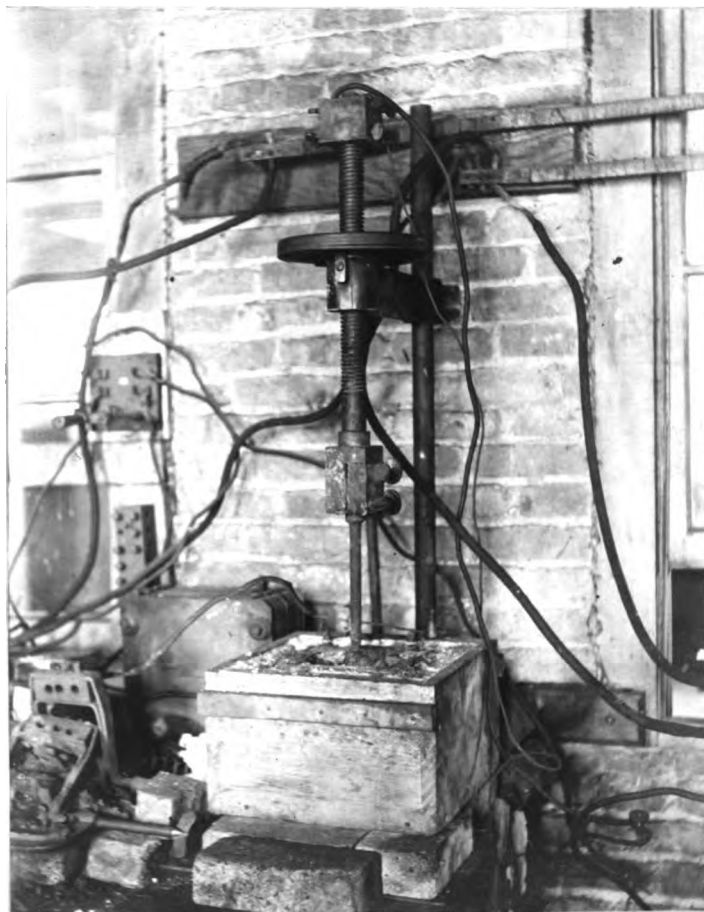






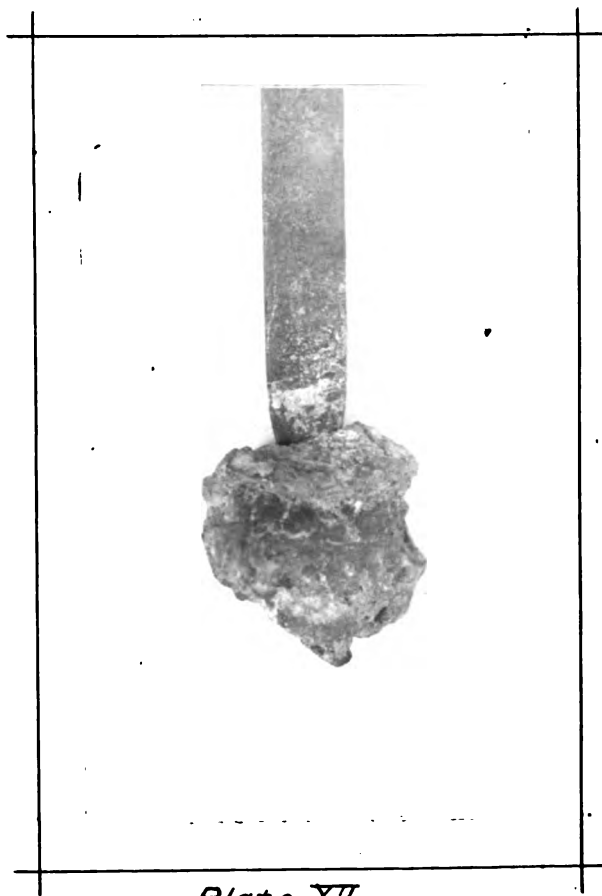
*Plate IX*  
*Dehydrated Bath. Undehydrated Bath.*  
*Black Portion has Cellular Structure Caused by*  
*been Electrolyzed. Bubbles of Hydrogen.*





*Plate XIII*  
*Apparatus No. 2.*





*Plate XII*  
*Calcium Deposit.*  
*Apparatus No. 2.*





*Plate X*  
*Longitudinal Section of Deposit.*

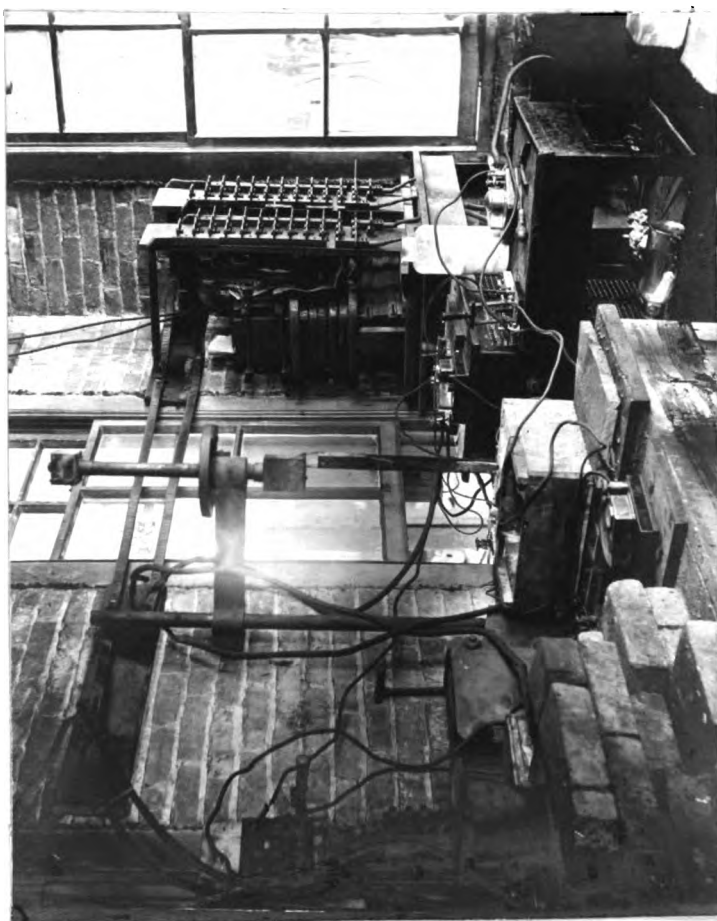






*Plate XI.  
Apparatus NaIII in Operation*





*Plate XIV*  
*Apparatus No. III*



Approved

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June 1/06.







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